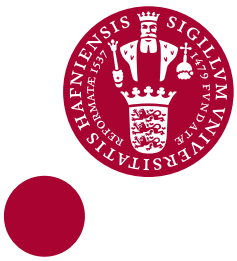

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Proton transfer in nonpolar solvents: An approach to generate electrolytes in aprotic media†

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Stabilizing charged species in nonpolar solvents is challenging due to their low dielectric constant. In contrast to formally ionic electrolytes, two series of acidic "potential" electrolytes have been developed in this study. These can be ionized by combining them stoichiometrically with a small molecule base in a typical nonpolar solvent, *n*-dodecane. The electrolytic conductivity of solutions of bis(2-ehtylhexyl)phosphoric acid was measured as mixtures with linear and branched dioctylamines and trioctylamines, and the solutions were found to become increasingly conductive as concentration increased, demonstrating that proton transfer occurred between the two species. Linear octylamines were found to be most effective at deprotonation. An acid-tipped poly(lauryl methacrylate) polymer ($PLMA_{48}$-COOH) was also studied to give a polymer soluble in *n*-dodecane with a single ionizable group located precisely at the end of the polymer chain. Trioctylamine could successfully deprotonate this acid group. Even in an aprotic solvent, the transfer of protons between acidic and basic moieties is a useful method for controlling the properties of dissolved molecules.

Acidic or basic small molecules and macromolecules are ubiquitous in water, and pH is a commonly used stimulus to vary the properties of chemicals in aqueous systems.[1–4] In nonaqueous solvents, the autoionization of the solvent, if protic, will be different to water, meaning that the ionization of these functional polymers will be different. In aprotic solvents, there will not be autoionizable protons, so solvent-solute proton transfer is not possible. The formation and stabilization of charges in nonpolar, low dielectric solvents is known to be challenging,[5] and so it is not surprising that identifying and synthesizing ionic species is challenging. Despite the challenge in producing ions, there are definite applications of such species in applications. Electrolytes in nonaqueous solvents are employed in many areas of the energy and materials sciences, such as specifically battery storage,[6–8] capacitors and supercapacitors,[7,9] solar energy conversion,[6,10] electro-optic displays,[6] and superabsorbent polymers.[11] Often surfactants are used to stabilize ions formed in nonpolar solvents,[12] and polymeric surfactants, such as polyisobutylene succinimide and its analogues,[13,14] can form ions via inverse micelle aggregates. These result in charge formation through self-assembled supramolecular species, though, not single molecules. There are few reports of macromolecules that are electrolytes in nonpolar solvents; only statistical copolymers of tetraalkylammonium ionic monomers and aliphatic monomers seem to have been studied previously.[15] These kinds of species, however, are "true electrolytes," with formal ionic species that do not require any additional components to form cations and anions. This is in contrast with "potential electrolytes," which form ions only when an additional species is added, such as a weak acid or base.[16] Acid-base electrolytes are of interest as their activity can be triggered by varying an external stimulus, such as a morphology change arising from a change in pH.[1,2,4] Although pH as a concept is meaningless in nonpolar solvents, proton transfer between acids and bases is possible and can result in the formation of ions.[17] In this communication, I develop an approach to producing ions in nonpolar solvents, both small molecules and macromolecules, through the selective ionization of acidic groups. The essential point is that these acidic molecules should only become ionic if and only if a basic molecules is added to deprotonate them. These results demonstrate that a method of producing ionic species that is common for water can also be used for nonaqueous solvents.

To identify a potential deprotonating agent, mixtures of a small-molecule acid, bis(2-ethylhexyl)phosphoric acid (DEHPA; Aldrich, 97%; **1**), were prepared with one of four small-molecule bases, bis(2-ethylhexyl)amine (DEHA; Aldrich, 99%;

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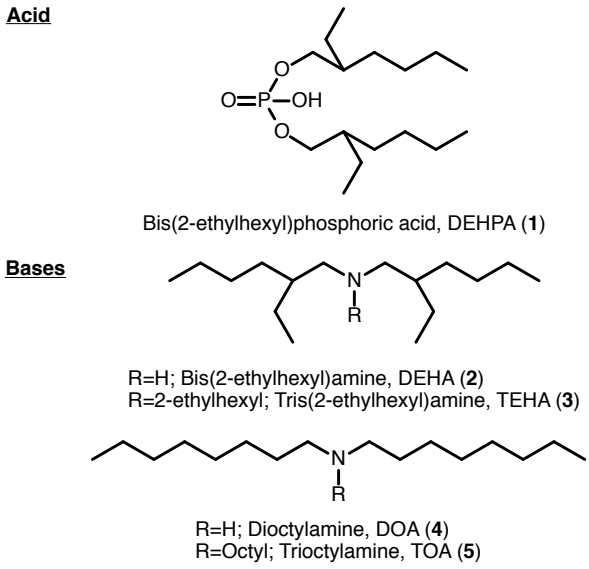


Scheme 1 Small-molecule acids and bases used for electrolytic conductivity measurements.

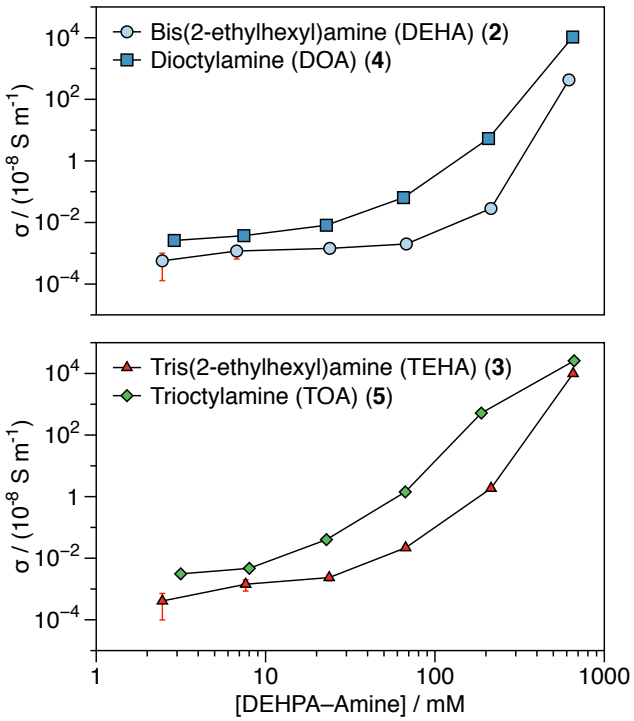
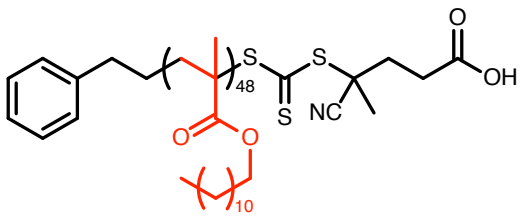


Fig. 1 Electrolytic conductivity (σ) of DEHPA (**1**) with different amine bases (**2**–**5**) as a a function of concentration. The octylamine bases are more powerful deprotonating agents than the (2-ethylhexyl)amine bases.

2), tris(2-ethylhexyl)amine (TEHA; Aldrich, $\geq$97%; **3**), dioctylamine (DOA; Aldrich, 97%; **4**), or trioctylamine (TOA; Aldrich, 98%; **5**), and the electrolytic conductivity was measured. All chemicals were used as supplied. The selected model acid and bases are shown in Scheme 1. The solutions were prepared as stoichiometric mixtures in *n*-dodecane (Sigma–Aldrich Reagent-Plus, $\geq$ 99%; stored over molecular sieves with a concentration of residual water of 6 ± 1 ppm[18]) at desired molar concentrations. Solutions were prepared by dissolving a measured mass of the solutes to a measured mass of *n*-dodecane with a total mass of $\sim$ 20 g. The molar concentrations were calculated using the molar mass of the solutes and the mass densities of the solutes, assuming ideal mixing. Molar units were used as these are typically used in studies of electrolytic conductivity.[19] Masses were measured using a GR-200 balance (A&D Company) with a reproducibility of $\pm$0.0001 g. This gives an uncertainty on the solution concentration of $>$ 1%.

These amines were selected to test the effect of the number of alkyl groups (diamine versus triamine) and the effect of chain branching (2-ethylhexyl versus octyl) on the efficacy of the bases on deprotonating the DEHPA. Aside from these systematic changes, the molecular size of the bases are maintained by using C_8 chains. Molecular volumes, calculated from the mass density and molar mass,[20,21] and sphere-equivalent radii, calculated from $r = \sqrt[3]{(3V)/(4\pi)}$, are given in the Supporting Information, Table S1. Electrolytic conductivity measurements were performed using a DT-700 nonaqueous conductivity probe (Dispersion Technology, Inc., USA). A glass cylinder with a diameter slightly larger than the probe was used to hold the solutions. The sample holder was cleaned thoroughly before measurements and rinsed thoroughly at the end with *n*-dodecane. The conductivity of *n*-dodecane was recored to ensure the cell was cleaned. Solutions were measured in increasing concentration, and the cell was washed with the next solution before the measurement performed. Measurements were performed at ambient laboratory temperature (22 °C). Ten measurements were performed using instrument optimized parameters for the conductivity, and the mean and standard deviation determined from these. The value of the conductivity (σ) for these solutions of DEHPA with all four small-molecule bases are shown in Figure 1. Proton transfer clearly occurs in these mixtures, and the electrolytic conductivity increases as a function of concentration due to the number of ions increasing. The electrolytic conductivity does not vary as a simple power law of the concentration ($\sigma \propto c^n$), which would be expected if there was a single dominant charge carrier. The species become ionized as a single pair of ions ($\sigma \propto c^{0.5}$ for single ions), but these surfactant-like molecules can self-assemble into inverse micelles in organic solvents ($\sigma \propto c^1$ for inverse micelles).[22,23] These acid-base mixtures are also known to act as proton conductors,[24] and this could also become the dominant mechanism at certain concentrations, resulting in a different power law dependence. Given the complex series of equilibria that give form the ions measured in a electrolytic conductivity measurement, it is not possible to model the data.

Although it is not possible to numerically determine the dissociation constants of the different species from the conductivity data, it *is possible* to qualitatively assess which of the bases is the more effective deprotonating agent. At all concentrations and for both the diamines and triamines, the octylamine bases have a higher electrolytic conductivity than the (2-ethylhexyl)amine bases. As the ions have essentially the same molecular volume,



$(PLMA)_n$–COOH (**6**): n = 48 ± 17

Scheme 2 Acid-tipped $PLMA_{48}$ synthesized by RAFT solution polymerization.

this means that the octylamine bases are more effective potential electrolytes. Therefore, these bases were studied further to see if they could be used to deprotonate an acid-tipped polymer in solution.

Poly(lauryl methacrylate) (PLMA) was synthesized via the reversible addition–fragmentation chain-transfer (RAFT) solution polymerization of lauryl methacrylate (Aldrich, 96%), in accordance with literature.[25–27] LMA (20.0 g), the RAFT CTA 4-cyano-4-(2-phenylethane sulfanylthiocarbonyl)sulfanylpentanoic acid (0.5 g; PETTC; synthesized in house[28,29]), and the initiator 2,2′-azobis(2-methylpropionitrile) (0.05 g; AIBN; Molekula) were dissolved in toluene (20.6 g; Fisher, HPLC grade). The vessel was sealed and then purged with nitrogen. The reaction was heated to 70 °C and allowed to proceed for 4 h. The crude polymer was precipitated into excess methanol to remove unreacted monomer. The purified polymer was characterized by ^{1}H NMR in CD_2Cl_2 (Cambridge Isotope Laboratory, 99.8 atom % D) and gel permeation chromatography (GPC) with tetrahydrofuran eluent against PMMA standards (^{1}H LMA conversion = 72%, ^{1}H LMA degree of polymerization (DP) = 48, GPC M_n = 10 600, **6**). The polymerization was well controlled, giving GPC dispersity of $Đ_M$ = 1.12 and standard deviation of $\sigma = 17$.[30,31] The structure of the polymer is shown in Scheme 2.

RAFT-synthesized PLMA is known to dissolve in *n*-alkane solvents.[25,26] Small-angle neutron scattering (SANS) on $PLMA_{48}$ in solution in *n*-dodecane show the polymer has a fractal surface in *n*-dodecane rather than being distributed as a Gaussian coil but that it can be well-described as a flexible cylinder, similar to other alkyl methacrylate polymers in solution.[18] Analysis of SANS data is discussed in the Supporting Information, Figure S1 and Tables S2–S3.

Solutions were prepared of dioctylamine and trioctylamine with $PLMA_{48}$-COOH (**6**) in a stoichiometric ratio in *n*-dodecane. The electrolytic conductivity values are shown in Figure 2. The magnitude of σ is several orders of magnitude less than for the DEHPA system, although the molar solution concentrations are also lower. There is also an immediately apparent difference between the two bases. The dioctylamine base (**4**) is unable to deprotonate the polymer to result in conductivity above the solvent baseline at the concentrations studied. The trioctylamine base (**5**), on the other hand, is able to deprotonate the polymer, giving rise to a detectable conductivity, which increases monotonically as a function of concentration.

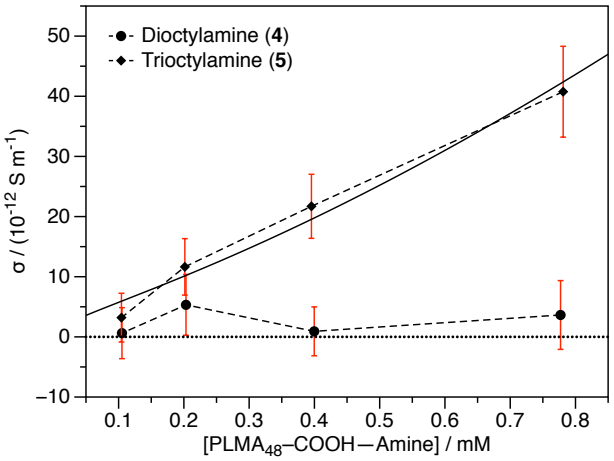


Fig. 2 Electrolytic conductivity (σ) of $PLMA_{48}$-COOH (**6**) with octylamine bases (**4**–**5**) as a a function of concentration. The dashed line shows a fit to the Fuoss–Krauss triple-ion theory.[32]

Unlike the DEHPA-amine system, it is possible to model the data of the solutions of $PLMA_{48}$-COOH and trioctylamine. The SANS data of the polymer in solution shows that the polymer is not present as collapsed aggregated multimers in *n*-dodecane. Therefore, a charged inverse micelle mechanism is not sensible. Given the low dielectric constant of the solvent ($\varepsilon_r = 2.0$),[33] there will be very strong interactions between the ionized species.[5,16] Therefore, the data have been fit to the model of Fuoss and Krauss who described the electrolytic conductivity as a sum of contributions from single ions and from triple ions.[32] The molar conductivity ($\Lambda = \sigma/c$) is a function of the infinite dilution molar conductivities of single ions and triple ions (Λ_0^s and Λ_0^t, respectively), the dissociation constants for single and triple ions (K_s and K_t). For such weak ions, Λ_0^s and Λ_0^t cannot be determined experimentally and instead have been calculated from the ion radii (sphere equivalent radii of the R_g of $PLMA_{48}$ and the volume of TOA).[34] Sphere-equivalent radii are used, in accordance with previous reports of ions in nonpolar solvents.[34–36] These are calculated from the molecular volume for the amine bases ($r = \sqrt[3]{(3V)/(4\pi)}$) and the radius of gyration R_g for the PLMA acid ($r = \sqrt{(5/3)} \cdot R_g$)[37]. The values were calculated to be $\Lambda_0^s = 1.4 \times 10^{-3}$ S m^2 mol^{-1} and $\Lambda_0^t = 9.1 \times 10^{-4}$ S m^2 mol^{-1}.

$$\Lambda = \frac{\Lambda_0^s \sqrt{K_s}}{\sqrt{c}} + \frac{\Lambda_0^t \sqrt{K_s}\sqrt{c}}{K_t} \qquad (1)$$

This form of the Fuoss–Krauss model assumes that equilibrium constants of cationic and anionic triple ions are equal, that activity coefficients and mobility corrections are equal to 1, and that ions form a small fraction of the total number ions.[32] If this model is appropriate for a system, a plot of $\Lambda\sqrt{c}$ as a function of c should give a straight line, from which K_s and K_t can be calculated. That is indeed the case for solutions of $PLMA_{48}$-COOH and TOA, whereas solutions of $PLMA_{48}$-COOH and DOA are not conductive within the resolution of the instrumentation. The plot and weighted fit to the data are shown in the Supporting Information,

Figure S2. In Figure 2, the values of the molar conductivity (Λ) are converted to the electrolytic conductivity (σ) by multiplying by the concentration c. The dissociation constant for single ion formation is very low ($(1.0 \pm 0.7) \times 10^{-16}$ mM) as is the value for triple ion dissociation ($K_t = 0.21 \pm 0.12$ mM), but this is typical for electrolytes in nonpolar solvents.[34] This emphasizes that ion formation is not strongly favored in low dielectric media, yet it is still achievable.

Why is a triamine able to act as a deprotonating agent but the diamine is not? It could either be a consequence of the sizes of the ions or the basicity of the amines. The molecular volumes, shown in Supporting information Table S1, of the two amines are very similar meaning that their radius on the scale of the Bjerrum length[16,38] in *n*-dodecane are also similar. The sizes of the ions, therefore, seem unlikely to dominate their efficacy as counterions. The ability of the amines to deprotonate an acid can be quantified computationally by their proton affinity, defined as the negative enthalpy change between a proton and a chemical species (the equilibrium shown in Equation 2).[39]

$$AH_n + H_3O^+ \leftrightharpoons AH_{n+1} + H_2O \quad (2)$$

This approach has been used to scale the effectiveness of ionic liquid ions previously.[40] Molecular structures were drawn in Avogadro,[41,42] and the structures optimized via molecular mechanics using the MMFF94(s) force field.[43] Computational chemistry calculations were performed using the Orca program.[44,45] The geometry was initially optimized using the PBE0 hybrid functional[46] with the ma-def2-SVP basis set,[47,48] followed by geometry optimization and frequency calculation using the ma-def2-TZVP basis[47,48] set to determine the non-electronic energy, scaled for the basis set.[49] Energies were then calculated using Møller–Plesset perturbation theory to the second order (MP2)[44] with the cc-aug-pVTZ basis set.[50,51] Output files are given in the Supporting Information. The proton affinity of the acetate anion, a model small molecule for the PETTC acid group, was determined to be 759 kJ mol^{-1}, in good agreement with literature calculations.[40] This makes a carboxylic acid group a moderate ionic liquid anion.[40] The calculated proton affinities for dimethylamine (241 kJ mol^{-1}) and trimethylamine (260 kJ mol^{-1}) are similar, yet greater for the trimethylamine. This is exactly what would be expected for a stronger deprotonating agent: it would have a greater affinity for protons. This suggests the molecular properties that would need to be targeted for macromolecular acid-base electrolytes. For anionic macromolecules and cationic counterions, the polymer end group needs to have a minimal proton affinity and the small molecule a maximal proton affinity and, for cationic macromolecules and anionic counterions, vice versa. Undertaking a comprehensive study of acids and bases with different functionality in the future would be an interesting extension of these results to see how the molecular properties relate to the ionic dissociation.

Despite it being difficult to produce and stabilize ions in nonpolar solvents, it is possible to produce ions with a measurable electrolytic conductivity in a typical nonpolar solvent, *n*-dodecane, using the transfer of a proton between an organic acid and base. This results in a system where the molecules only become ionic when selectively combined, offering the ability to control their functionality. In particular, using RAFT chemistry to synthesize a soluble PLMA polymer has enabled the acid functionalization of the macromolecule. The single carboxylic acid moiety means that the polymer is ionizable on *precisely* one site at *precisely* the end of the polymer chain. No previous ionizable macromolecular in a nonpolar solvent possesses this level of control.[15] The acidic nature of the functional moiety means that the ionization can be triggered by the addition of an organic base; in this case, trioctylamine was found to be an effective deprotonating agent. While this is not reversible like a pH change in water, to achieve controllable ionization due to an acid-base reaction in a non-autoionizable, aprotic solvent is gratifying. Although the ion dissociation constant is low for this PLMA macromolecular electrolyte, this demonstration that proton transfer between acids and bases can be achieved in a nonpolar solvent suggests that optimization of the two "potential" ions in the future would be desirable, either through modifying the strength of the RAFT CTA acid or the small-molecule base. Future work to on a wider range of acid and basic moieties should make it possible to determine the relationship between molecular structure and electrolyte strength.

Conflicts of interest

There are no conflicts to declare.

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